Lithium Batteries with Higher Capacity and Voltage

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The University of Texas at Austin

Date

Project ID # ES325

OVERVIEW

Timeline

- Project Start Date: 4/16/15
- Project End Date: 6/30/17
- Percent Complete: 50%

Barriers

- Cost
- Safety
- Performance
- Life

Budget

- Total project funding: $348,000
  - DOE Share: $174,000
  - Contractor Share: $174,000
- Funding FY 2016: $174,000
- Funding for FY 2017: $174,000

Relevance/Objectives

- Objective:
  - To develop an electrochemically stable alkali-metal anode that can avoid the SEI layer formation and the alkali-metal dendrites during charge/discharge. To achieve the goal, a thin and elastic solid electrolyte membrane with a Fermi energy above that of metallic Li and an ionic conductivity $\sigma > 10^{-4}$ S cm^{-1} (1) will be tested in contact with alkali-metal surface. (2) The interface between the alkali-metal and the electrolyte membrane should be free from liquid electrolyte, (3) have a low impedance for alkali-metal transport and plating, and (4) keep a good mechanical contact during electrochemical reactions.
- Impact:
  - An alkali-metal anode (Li or Na) would increase the energy density for a given cathode by providing a higher cell voltage. However, lithium is not used as the anode in today's commercial lithium-ion batteries because electrochemical dendrite formation can induce a cell short-circuit and critical safety hazards. This project is to find a way to avoid the formation of alkali-metal dendrites and to develop an electrochemical cell with dendrite-free alkali-metal anode. Therefore, once realized, the project will have a significant impact by an energy-density increase and battery safety; it will enable a commercial lithium-metal rechargeable battery of increased cycle life.
  - Our key approach is to introduce a solid-solid contact between an alkali metal and a solid electrolyte membrane. Where SEI formation occurs, the creation of new anode surface at dendrites with each cycle causes capacity fade and a shortened cycle life. To avoid the SEI formation, a thin and elastic solid electrolyte membrane would be introduced, or the solid electrolyte should not be reduced by, but should be wet by, a metallic alkali-ion anode.

Milestones

FY 17 Milestones:

- Demonstrate the cycle life and capacity of a Li-S cell-**Completed (2017)**
- Demonstrate a high-voltage cell containing the glass electrolyte-**(Completed March 2017)**
- Demonstrate a new battery concept-**Completed (2017)**
- Test energy density, cycle life, rate of charge/discharge of the new battery concept **Ongoing (2017-2018)**

FY 17 Deliverables

- Coin cells that are safe and low-cost with a long cycle life at a voltage $V > 3.0$ V

Approach

- Approach: Design, make and test cells
- Out-Year Goals: Coin cells that are safe and low-cost with a long cycle life at a voltage $V > 3.0$ V.
- Collaborations: A. Manthiram, UT Austin, and Karim Zaghib, Hydro Quebec

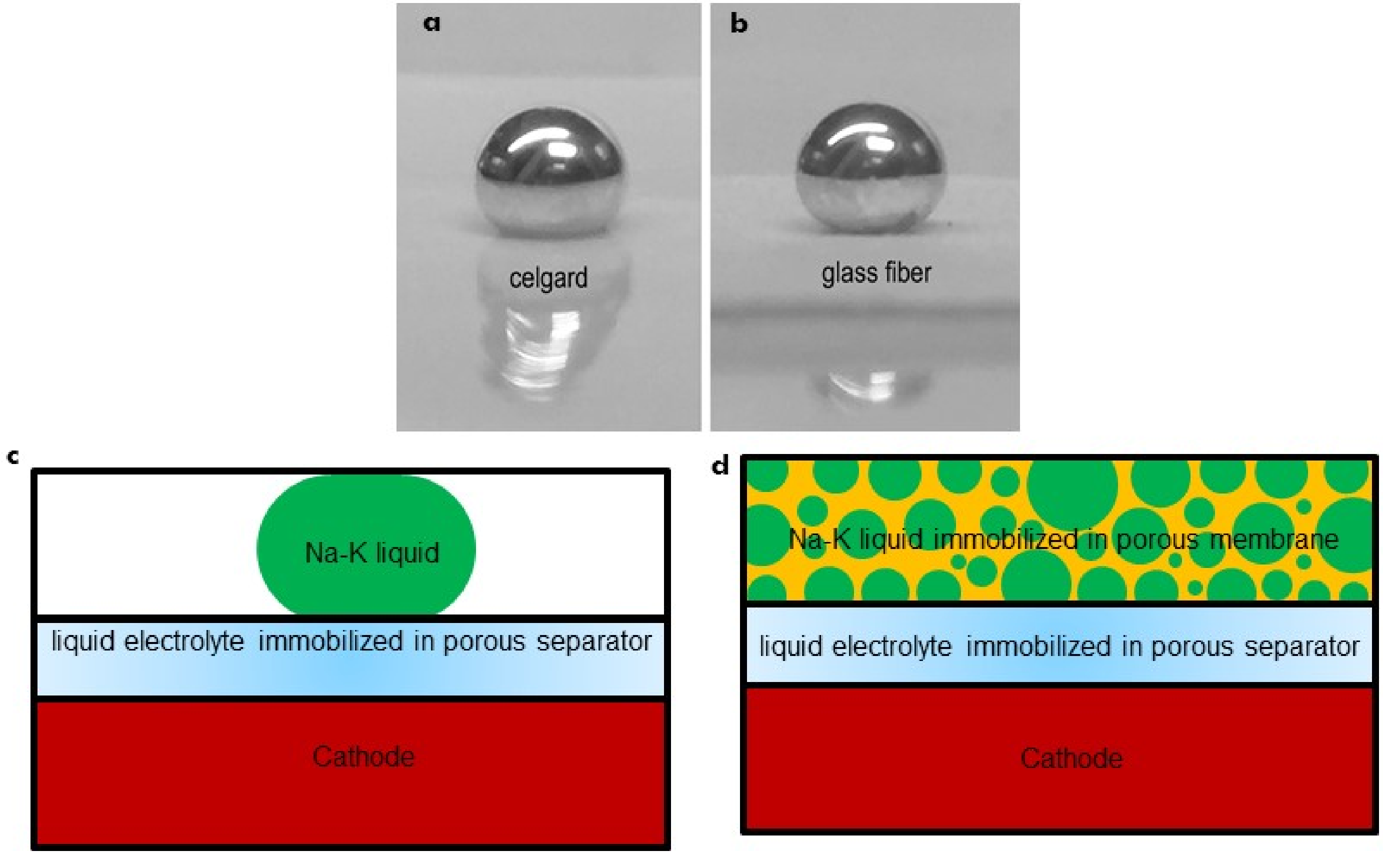
Technical Accomplishments

- Shown a solution to safe alkali-metal anode
- Introduced alternative cathode strategies
- Provided a pathway to competitive electric road vehicles

Responses to Previous Year Reviewers Comments

Work not reviewed as it as presented as a poster, not in a lecture last year.

Dendrite-Free Alkali-Metal Plating



Leigang Xue *et al.*

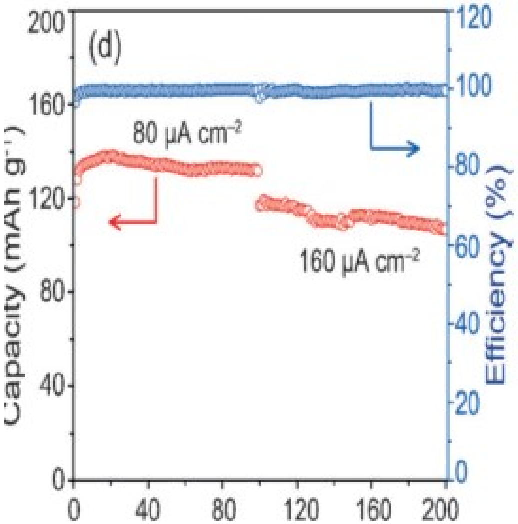
Garnets with $E_C \simeq E_F(Li)$

- $Li_7La_3Zr_2O_{12} \cdot Al^{3+}$: $\sigma_i \approx 10^{-4}$ S cm^{-1} (Weppener)
- $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12} \cdot Al^{3+}$: $\sigma_i \approx 10^{-3}$ S cm^{-1} at 25°C

- Problems:
  Hygroscopic grain boundaries
  Dendrite penetration of grain boundaries

2 wt% LiF
Stabilizes against moisture

Li/Polymer/LLZT: $2LiF/LiFePO_4$



Rhombohedral $LiZr_2(PO_4)_3$

Preparation:

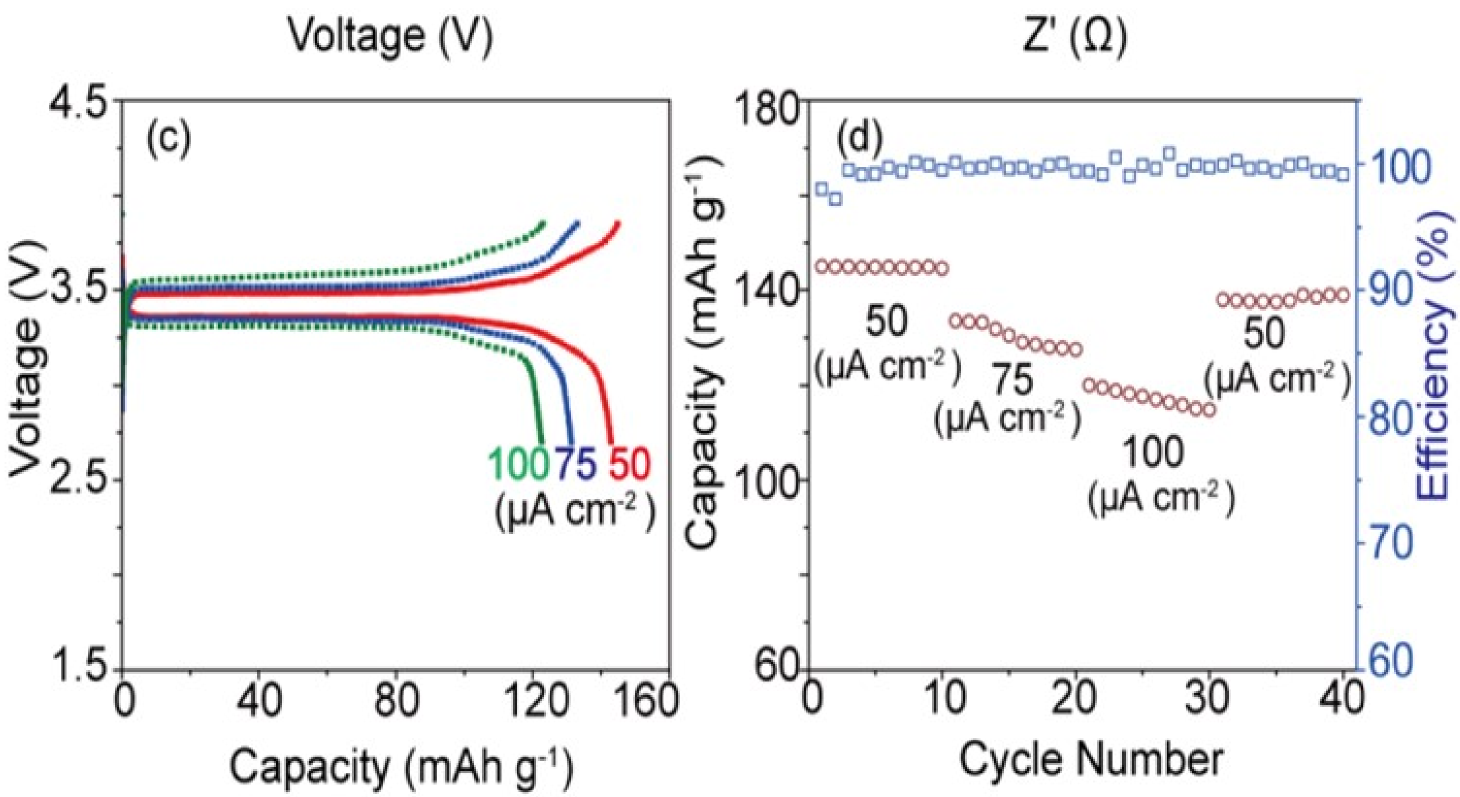
- With Zr-acetate precursor, rhombohedral $LiZr_2(PO_4)_3$ forms at 900°C
- Dense Polycrystal pellets obtained at 1000°C with SPS
- Lithium wets $LiZr_2(PO_4)_3$ at 350°C forming stable, Li^+ conductive, amorphous interphase layer

Properties:

- $\sigma_{Li} = 1 \times 10^{-4}$ s cm^{-1} at 25°C
- $\Delta H_m = 0.28$ eV
- Li^0 dendrite-free plating with R_{ct} 0.50 Ω at 80°C

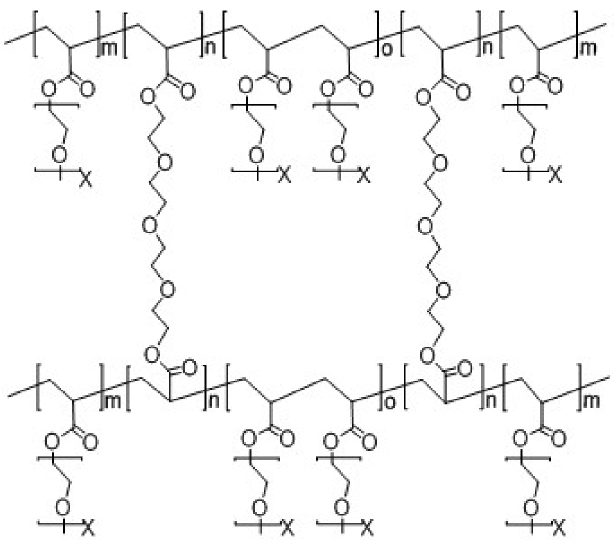
Yutao Li *et al.* PNAS **113**, 13313, (2016)

Li/$LiZr_2(PO_4)_3$/$LiFe(PO_4)$



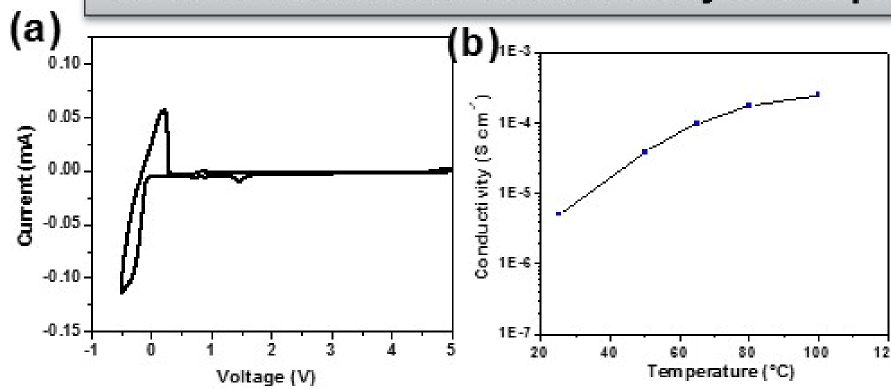
Yutao Li *et al. PNAS,* **113**, 13313 (2016)

Cross-linked polymer

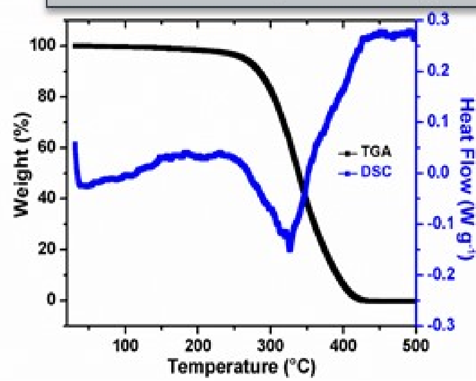


CPMEA

CV curve and ionic conductivity of the polymer

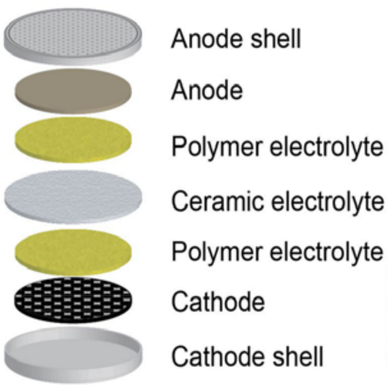


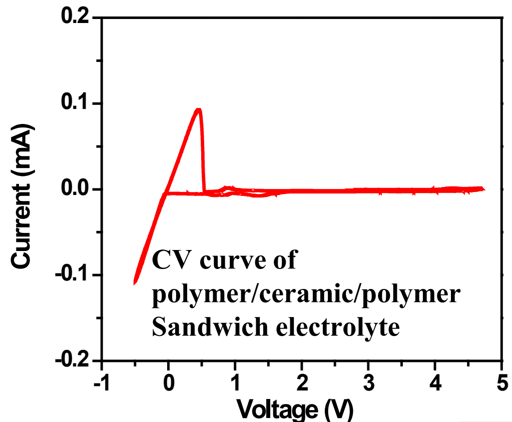
TGA and optic image of the polymer

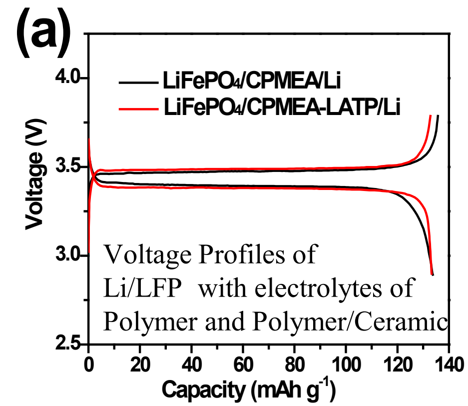


Weidong Zhou, Shaofei Wang, Yutao Li and John B. Goodenough *J. Am. Chem. Soc.* **2016**, 138, 9385–9388.

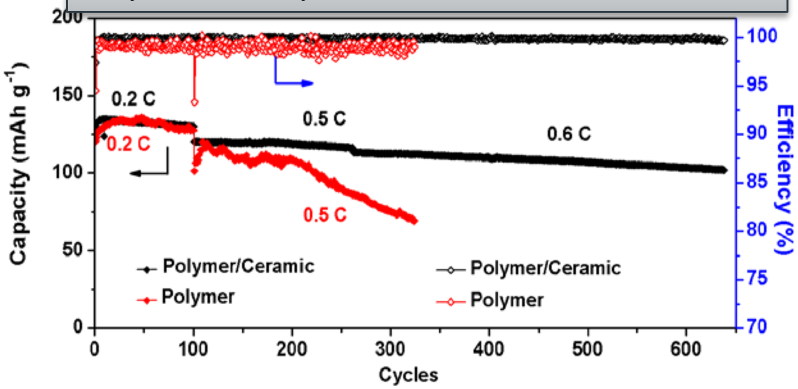
Polymer/Ceramic/Polymer Sandwich Electrolyte



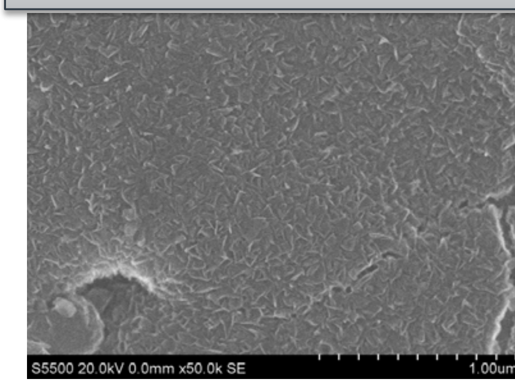




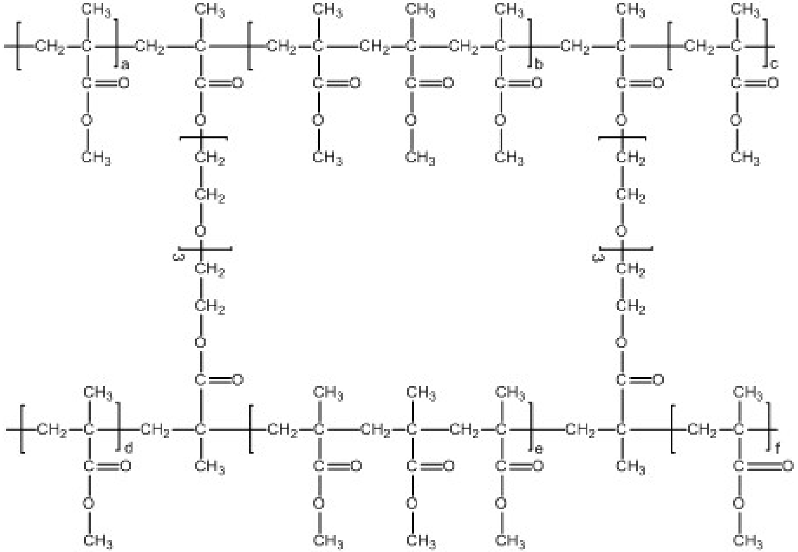
Cycling performance of Li/LFP with electrolytes of Polymer and Polymer/Ceramic



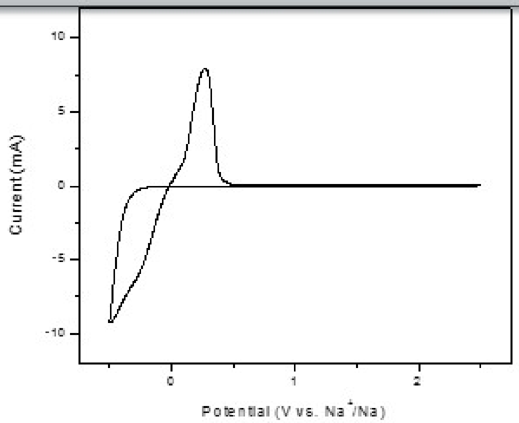
SEM image of lithium metal after cycling **No Dendrites**



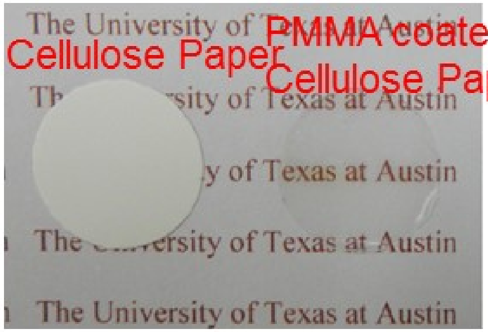
Cross-linked PMMA



Reversible sodium plating/stripping

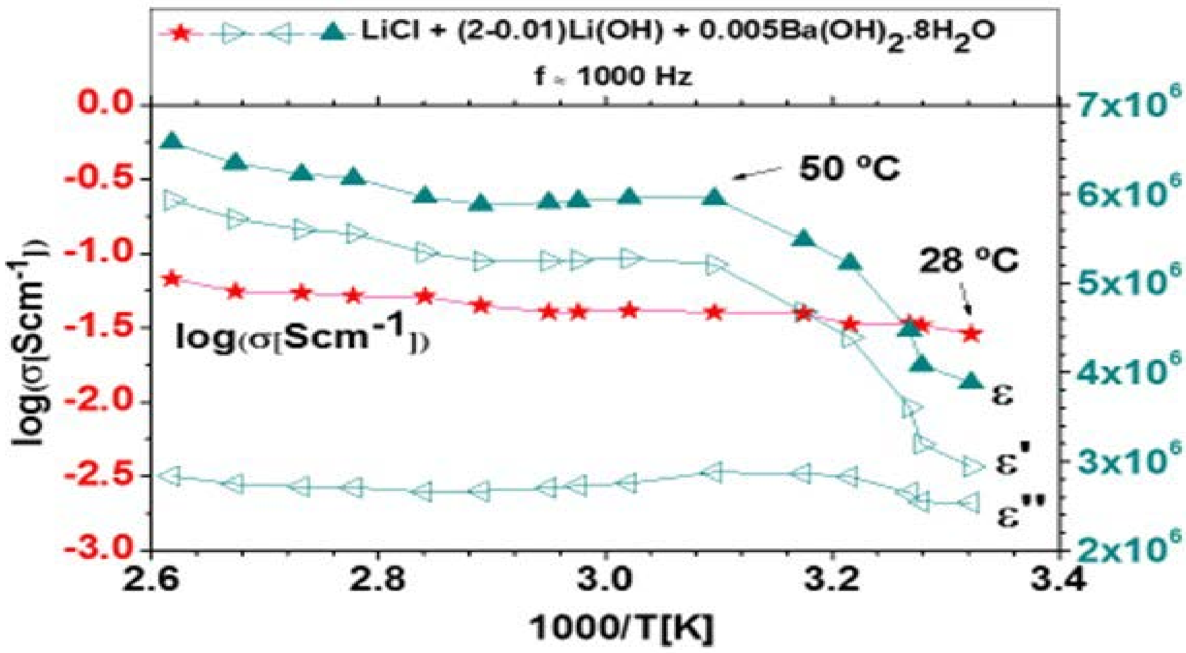


PMMA on cellulose paper



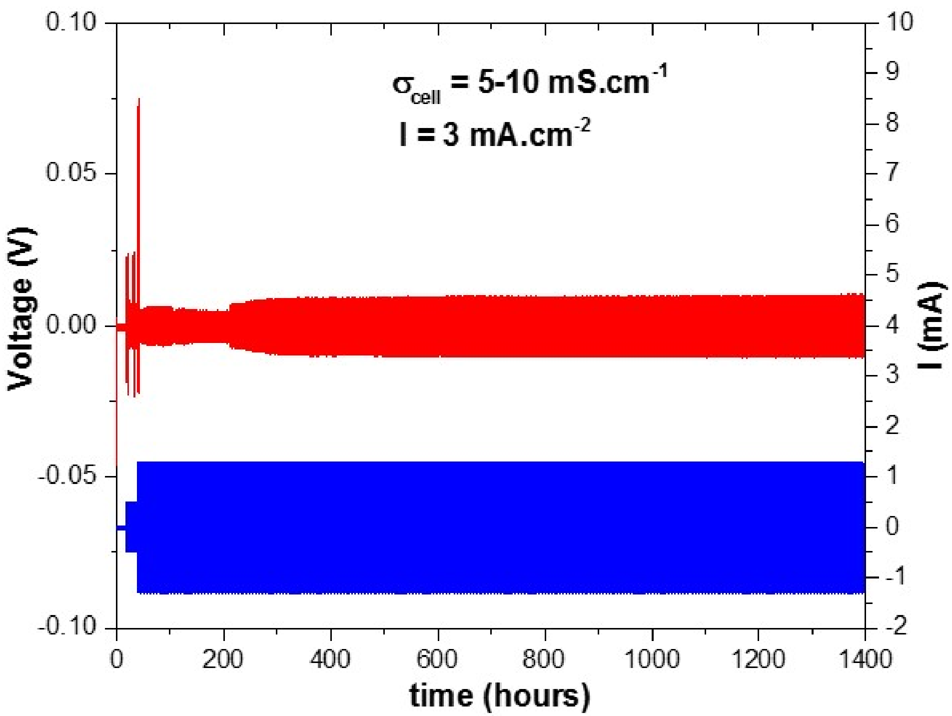
Hongcai Gao, Weidong Zhou, Kyusung Park, and John B. Goodenough *Adv. Energy Mater*. **2016**, 6, 1600467.

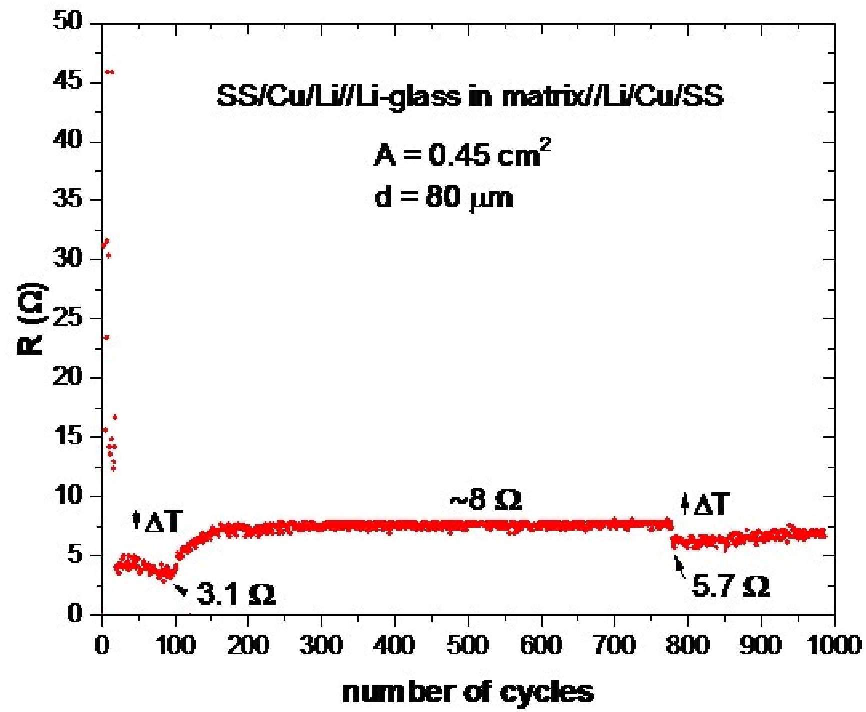
Arrhenius plots of Li^+ *ac* conductivity and permittivity at 1000 Hz of a Li-Glass



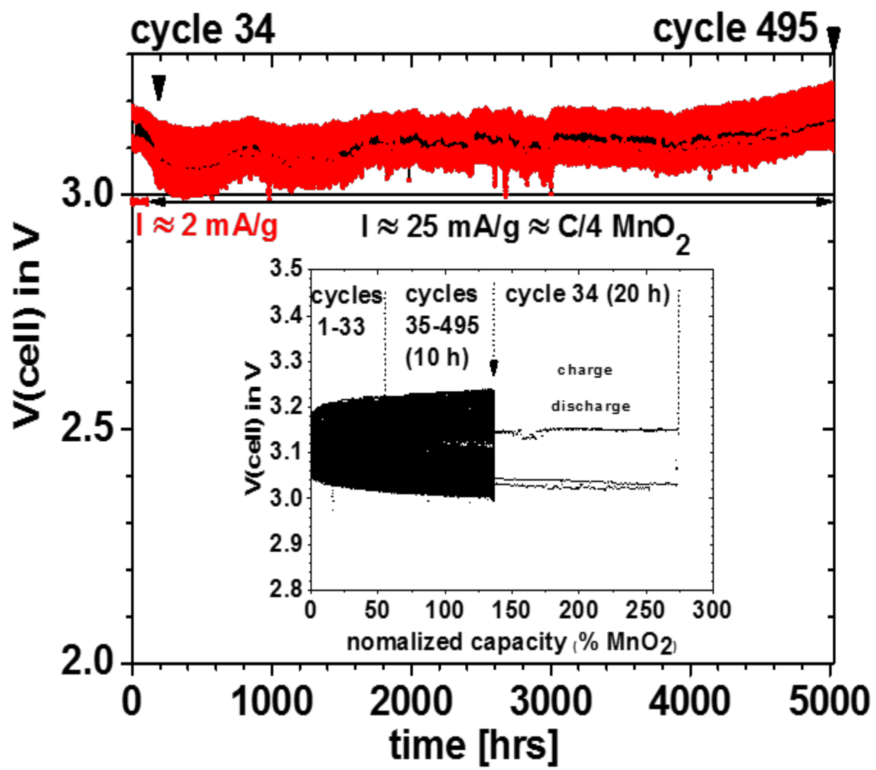
M. Helena Braga, University of Porto, Portugal

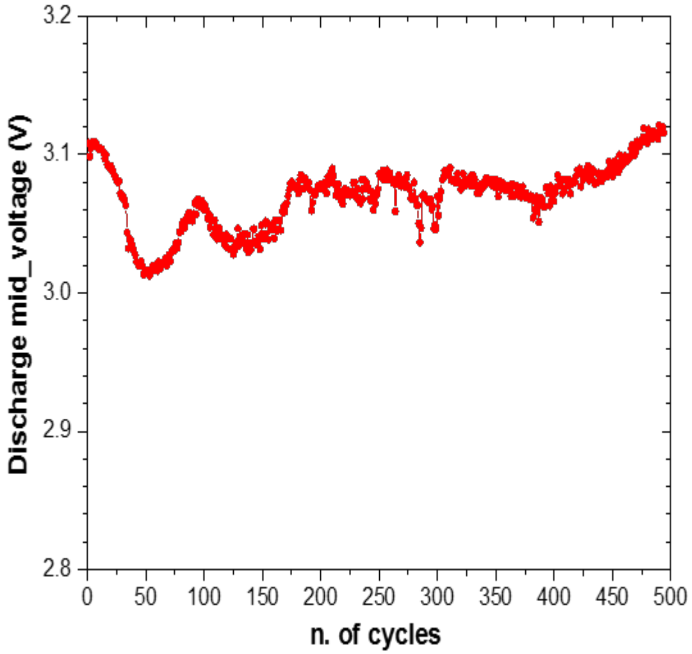
Symmetric Li/Li-glass/Li cell (Glass σ_{Li} = I5 S cm^{-1} at 25°C



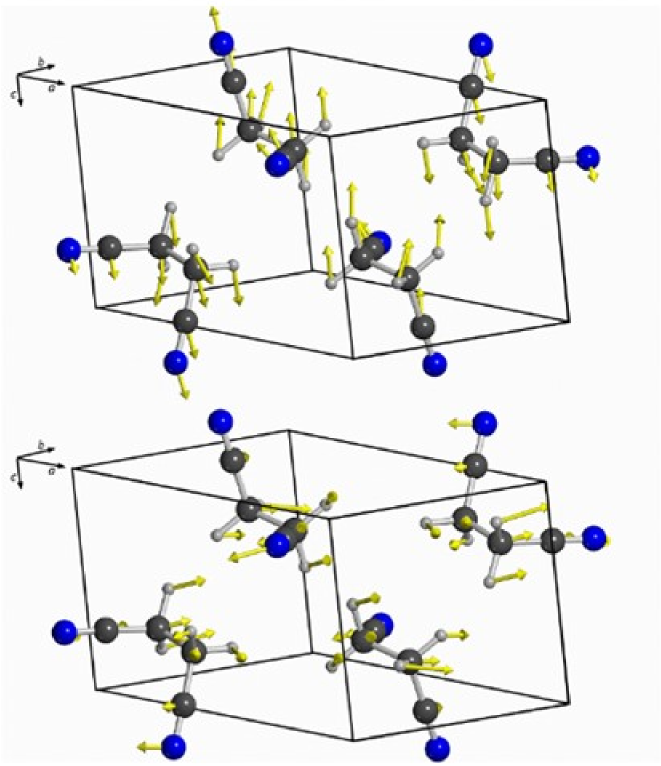


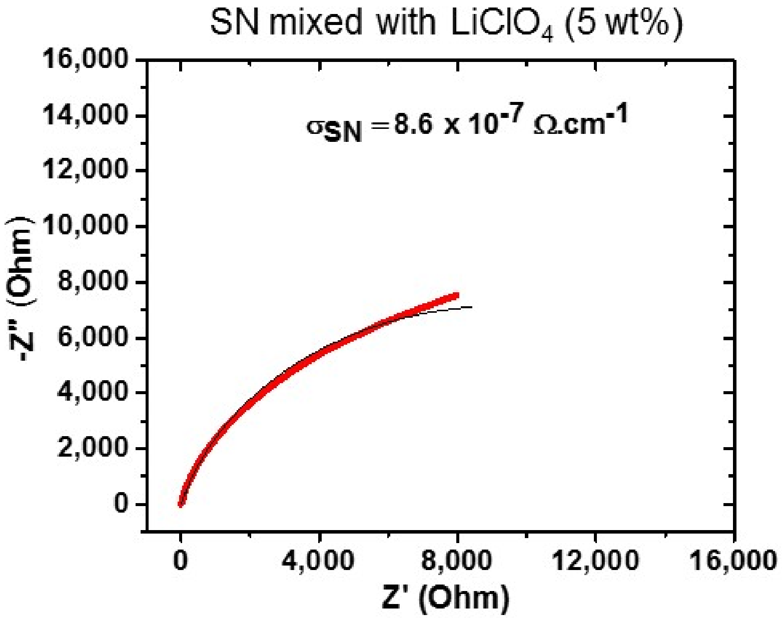
Li/Li-glass/γMnO_2-C-Cu





Succinonitrile (SN)



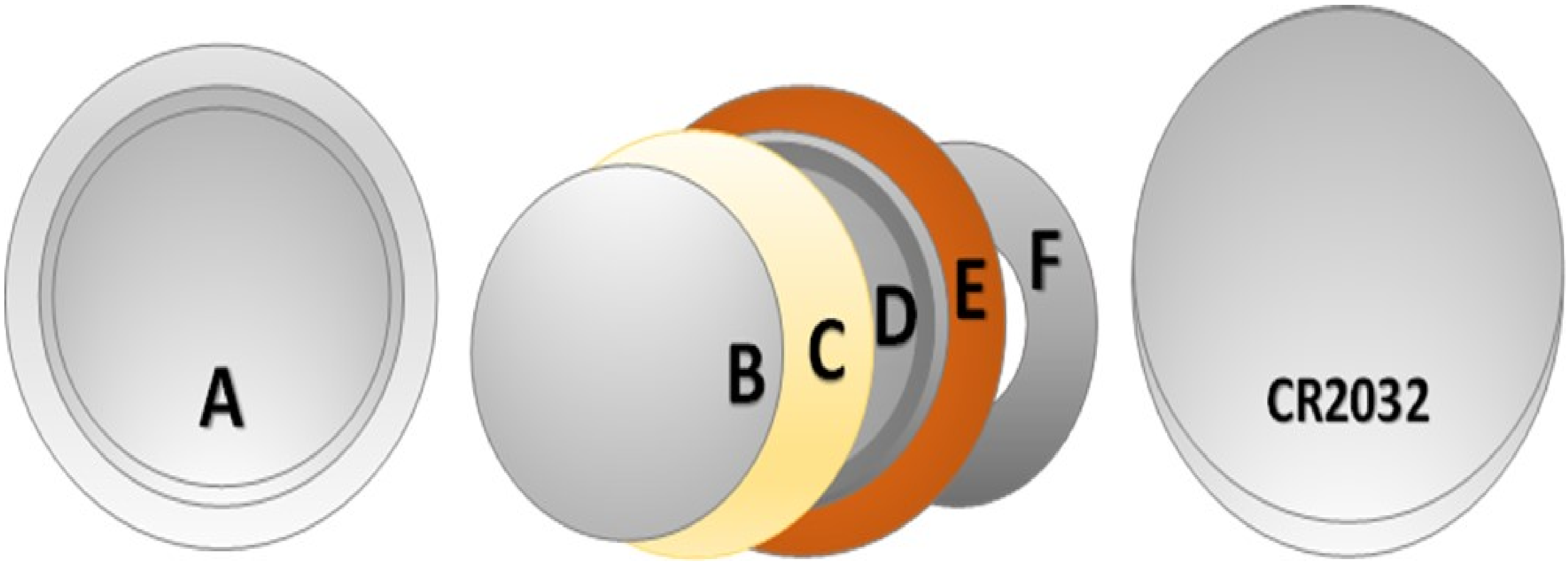


Terahertz vibrational modes of the rigid crystal phase of succinonitrile.

D. V. Nickel, S. P. Delaney, H. Bian, J. Zheng, T. M Korter, D. M Mittleman, The journal of physical chemistry. A, 2014

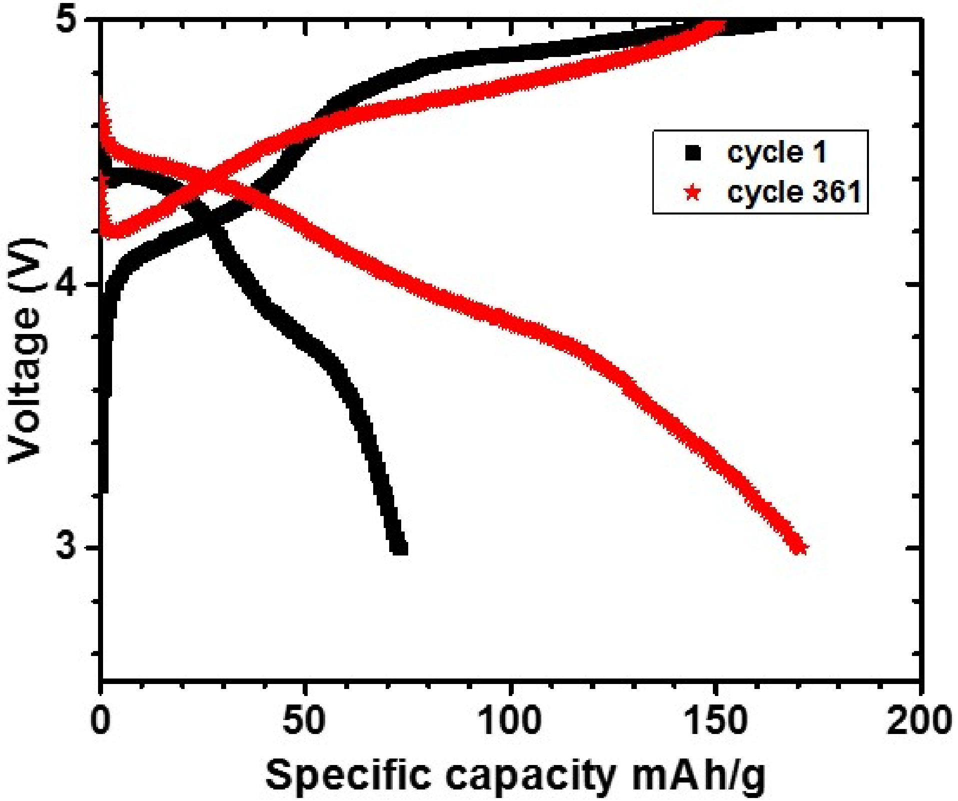
High-Voltage Solid-State Cell

$\text{Li-NMO} = \text{Li}[\text{Li}_x\text{Mn}_{1.5\text{-}y}\text{Ni}_{0.5\text{-}2}]\text{O}_{4\text{-}x\text{-}\delta}\text{F}_x$, $x = (y + z) \approx 0.36$



A – cell's shell; B – Li metal; C – glass electrolyte in non-woven paper matrix, D – succinonitrile/Li-NMO/Carbon in Al (double carbon coated), E – Cu spacer; F – spring.

Cycling between 3.0 and 5.0 V



Remaining Challenges

- Optimizing capacity of plated cathodes
- Demonstrate alternative alkali-metal rechargeable cells
- Determine roles of electrolyte electric dipoles
- Broader application

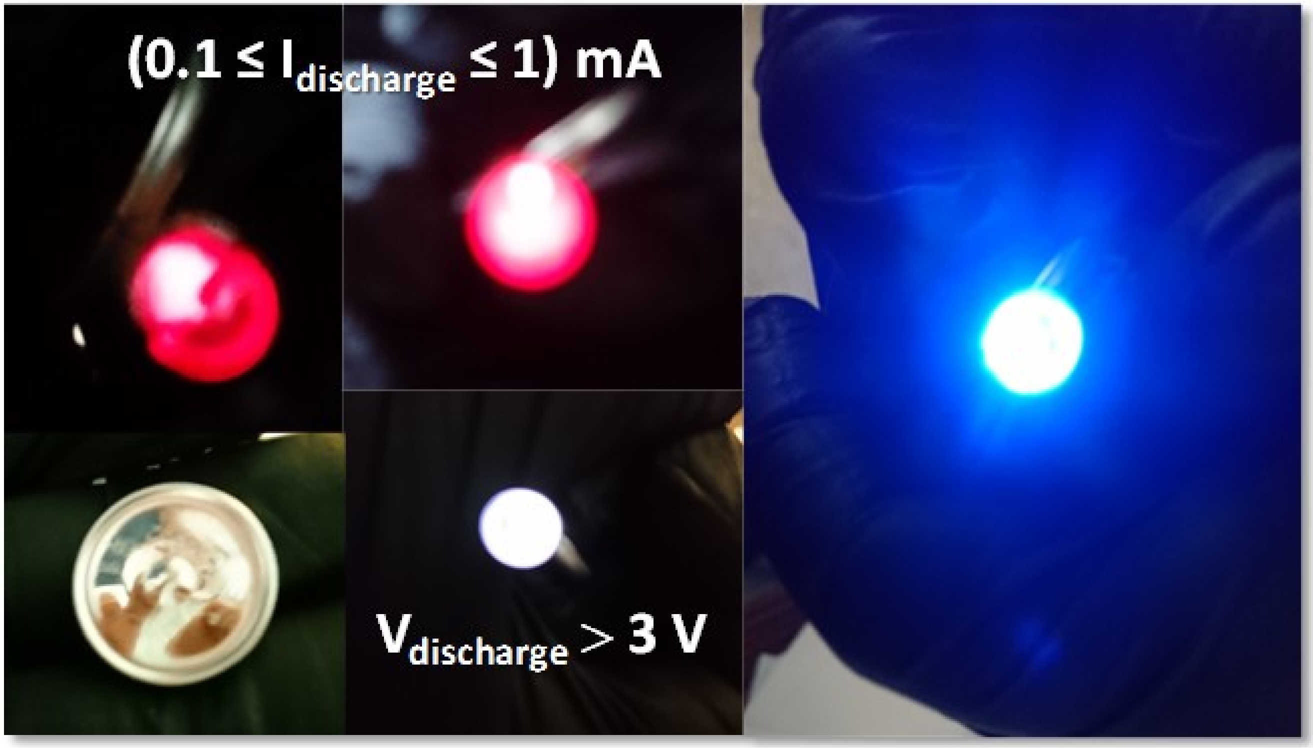
Summary

Comparisons of ceramic, polymer, plasticizer, and glass electrolytes have:

- Shown a solution to safe alkali-metal anodes
- Introduced alternative cathode strategies
- Provided a path to competitive electric road vehicles.

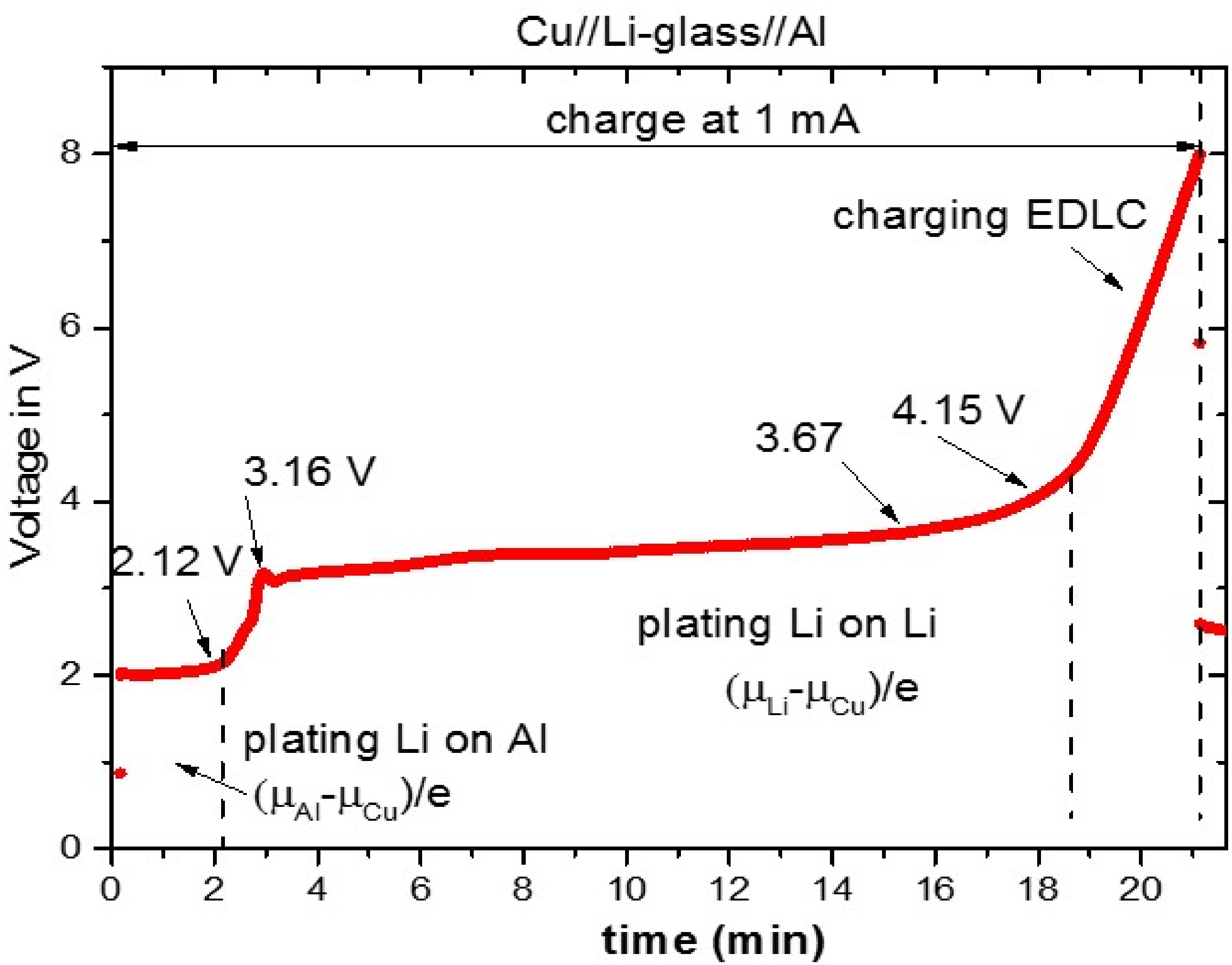
Back up Slides

LEDs Lit with the Solid-State Cells



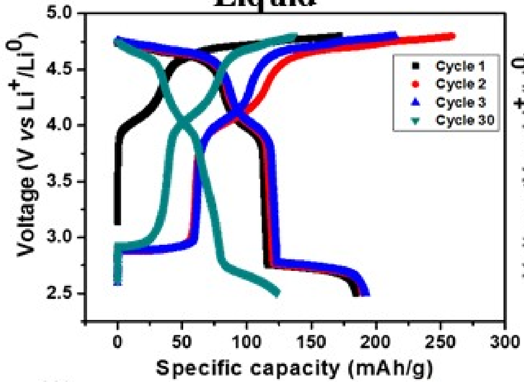
Voltage and current profiles that were met.

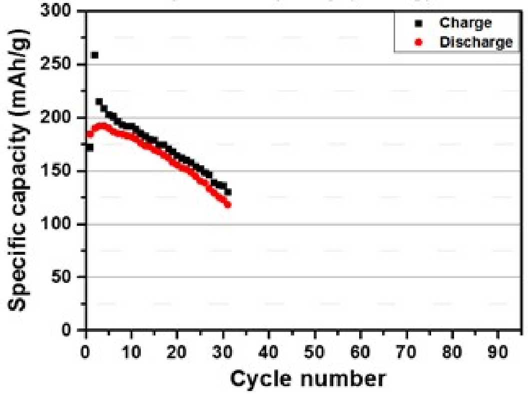
Cu/Li-glass/Al Cell



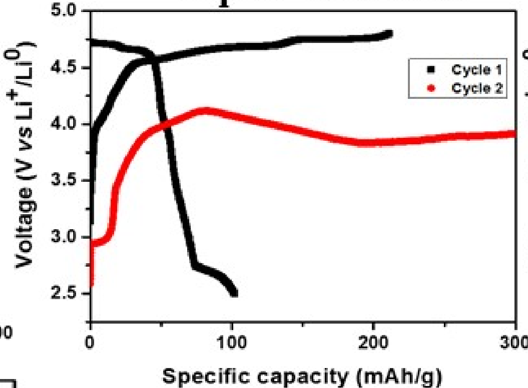
Charge/Discharge Cycles with Different Electrolytes

Liquid

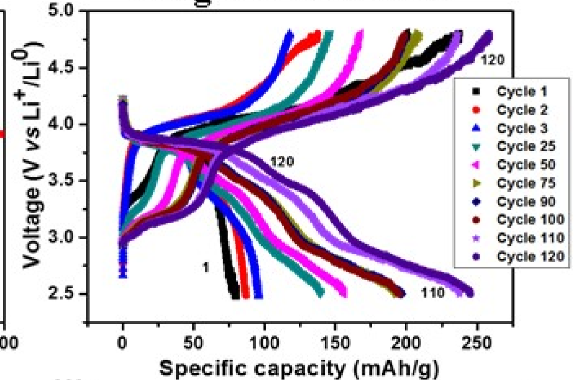


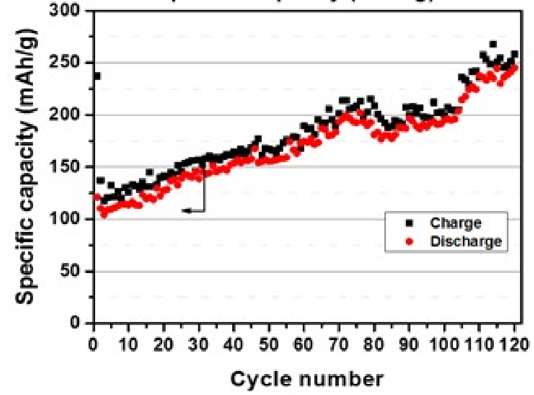


Liquid/ Plasticizer



Li$^+$-glass/ Plasticizer





Impedance Spectra of a Spinel/Li Cell